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14. ABSTRACT

Stabilizers for Glycidyl Azide Polymer (GAP) and GAP-based propellants were evaluated by Atlantic Research Corporation (ARC) and 3M (subcontract). The objectives of the program were: 1. to determine the stability of GAP; 2. to document the effect of propellant ingredients on GAP stability; and 3. to demonstrate stabilizers that hinder or block the major decomposition pathways of GAP and GAP Propellants in order to improve long term storage stability.

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STABILIZERS FOR GAP AND GAP-BASED PROPELLANTS
INTERIM REPORT

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ABSTRACT

Stabilizer(s) for Glycidyl Azide Polymer (GAP) and GAP-based propellants were evaluated by Atlantic Research Corporation (ARC) and 3M (subcontract). The objectives of the program were: 1. to determine the stability of GAP; 2. to document the effect of propellant ingredients on GAP stability; and 3. to demonstrate stabilizers that hinder or block the major decomposition pathways of GAP and GAP propellants in order to improve long term storage stability.

Model compounds simulating the azido-bearing functional units of GAP (azide adjacent to polyether backbone, azide adjacent to terminal hydroxyl, and azide adjacent to urethane cross-link) were manufactured by 3M to study the thermal and photolytic decomposition pathways of GAP. Thermal stability of the azide group was shown to be independent of location on the GAP molecule.

Compounds known to destabilize organic azides (i.e., certain transition metals, and protic or Lewis acids) were combined with GAP model compounds and GAP prepolymer to simulate the destabilizing influence of candidate propellant ingredients. Potential stabilizing compounds were combined with the "destabilized GAP" mixtures to test effectiveness. Stabilizer groups of promise included metal scavengers, epoxy compounds, and acid scavengers.

Selected stabilizers were evaluated in aging studies using GAP-based reduced-smoke and minimum-smoke binder systems (i.e., no solid oxidizers or fuels added). In each binder system, the effects of fumed alumina, Protech 8725, and DER-331 were compared to an unstabilized (baseline) binder. Aging tests included uniaxial tensile properties, dimensional stability in 2" cubes, off-gassing, stabilizer depletion, and burning rate. After 3 months accelerated aging, stabilized binders exhibited lower rates of nitrogen off-gassing. They also exhibited more-stable tensile and sol/gel properties. Tests of the 6-month accelerated-aging samples are pending.

INTRODUCTION

The thermal decomposition of organic azides such as GAP has been shown to proceed catalytically in the presence of certain transition metal species and protic or Lewis acids [7,10]. Decomposition initiates with the release of a nitrogen molecule followed by the formation of a highly reactive nitrene-intermediate. The nitrene probably rearranges to an imine through a 1,2 hydrogen shift (Figure 1).

$$R - CH_2 - N_3 \quad \xrightarrow[-N_2]{\Delta} \quad R - CH_2 - \ddot{N}: \longrightarrow R - CH = N - H$$
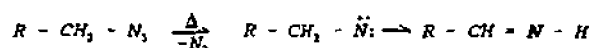
Figure 1. Decomposition Scheme for Organic Azides

The stability of GAP binder in propellant-aging studies has varied according to the lot of GAP used. This variability may be linked to residual impurities from the synthesis process [3,8].

Historically, GAP has shown excellent stability in certain propellants, but poor stability in others [1,6,8,11]. Poor stability is manifested by high rates of nitrogen off-gassing and associated grain fissuring and cracking. Stability appears closely linked to the chemical properties of the other propellant ingredients, particularly those containing acidic or certain transition metal complexes. Ammonium perchlorate and ammonium nitrate are salts of strong acids and may contain acid residues. Ammonium nitrate may contain partially-soluble zinc, nickel, or copper complexes used in phase stabilization. Many propellant cure catalysts for urethane systems are based on soluble organo-metallic complexes. Iron-, lead-, or copper-based burning rate catalysts are also commonly used. Thus, destabilizing species are present in both the GAP itself and in many propellant ingredients. Effective stabilizers should act to block decomposition pathways in either case.

DISCUSSION OF RESULTS

MODEL COMPOUNDS

Prior to the subject program, 3M manufactured model compounds that simulated azide-functional regions of GAP [4]. The regions simulated included azides adjacent to hydroxyl end-groups, azides adjacent to the polyether backbone, and azides adjacent to urethane-cross-links (Figure 2).

$$\begin{bmatrix} CH_3 - CH - O \\ \quad | \\ \quad CH_2 \\ \quad | \\ \quad N_3 \end{bmatrix} \qquad CH_3OCH_2CH-OH \\ \qquad\qquad\qquad | \\ \qquad\qquad\qquad CH_2 \\ \qquad\qquad\qquad | \\ \qquad\qquad\qquad N_3$$

$$\begin{matrix} & & O \\ & & \| \\ CH_3OCH_2CHOC & - & NH - C_4H_9 \\ | \\ CH_2 \\ | \\ N_3 \end{matrix} \qquad\qquad \begin{matrix} N_3CH_2CH_2OCH_2CHOCH_3 \\ | \\ CH_2 \\ | \\ N_3 \end{matrix}$$

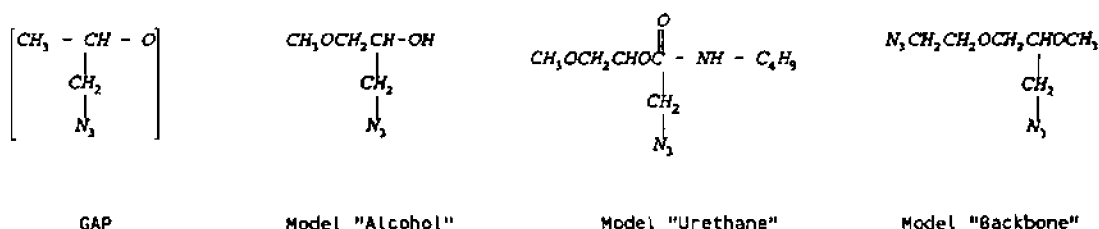GAP   Model "Alcohol"   Model "Urethane"   Model "Backbone"

Figure 2. Model Compounds Simulating Azide Functional Regions in GAP

Model compounds were made available to the program for the purpose of investigating thermally-induced decomposition mechanisms of GAP. Of interest were the relative rates of azide decomposition as a function of position in the GAP molecule and the decomposition products associated with specific azide locations. Model compounds were of special interest in the latter case, where it was hoped that identification of decomposition products would be made simpler by virtue of a simple and well-defined parent compound.

Thermal decomposition rates of the model compounds and GAP were determined through measurement of nitrogen evolution during extended exposure at 105 to 125 degrees C. Initial results suggested that proximity of a urethane group produced faster rates of nitrogen off-gassing. Subsequent studies , however, showed this to be an artifact of the low-molecular-weight urethane model. Work with higher-molecular-weight urethane models showed that the rate of azide decomposition was essentially independent of location within the GAP molecule. The decomposition rates of the model compounds approximated those of GAP (see Table I). Decomposition rates under air were slower than under argon atmosphere.

Table I. Decomposition Rates for GAP and Model Compounds

Compound Type	Decomposition Rate (10^3 Hr^{-1})		E (Kcal/mole)
	Temp = 125 C	Temp = 105 C	
GAP (Lot 9961)	0.22	0.02	37
Urethane (Butyl-NCO)	2.48	0.52	23
Diethoxy	0.45	0.17	15
Alcohol	0.78	0.08	34

Isolation and identification of decomposition products met with partial success. The urethane model appears to decompose into dimers and trimers of the parent compound, less the azide group. The diethoxy (backbone) model compound decomposed more slowly than the urethane model to form a low percentage mixture of polymeric imines or carboxamide in the parent compound. The decomposition rate of the alcohol model compound was the slowest of the three compounds. Products were volatile and could not be successfully separated from the parent compound.

STABILIZER SCREENING IN MODEL COMPOUNDS

Over 30 potential stabilizers were selected from several classes of materials including metal chelating agents, proton scavengers, and surface active adsorbers. Compatibility and effectiveness of candidates in GAP-like materials were screened qualitatively based on discoloration and off-gassing characteristics of the urethane model compound in oven stability tests. Following down-selection of promising compounds, candidates were tested more extensively as to stabilizing ability and effects on cure rate and cure off-gassing in the other model compounds and in GAP prepolymer. The most positive results were obtained with Protech 2725 (a proprietary chelating agent from MACH I), certain epoxies, fumed alumina, and proton sponge. Details of the test results were reported by Denenholz and Manzara of 3M[2].

STABILIZER SCREENING IN GAP

Stabilizer effectiveness was investigated in GAP alone, in unfilled GAP gumstocks (binder components only), and in filled GAP gumstocks (oxidizers and rate modifiers added). Of immediate interest were the following:

1. stability of GAP itself (cured and uncured);
2. destabilizing effects of propellant ingredients/impurities;
3. stabilizer effects in GAP with destabilizing elements;
4. stabilizer effects on GAP cure reactions.

Results of the above investigations are discussed below.

Inherent stability of the four GAP lots available to the program and their relative rates of cure are summarized in Table II. GAP lot 9961 containing the lowest level of residual tin impurity was found to be the

most stable, and not surprisingly, exhibited the slowest rate of cure. The relative stability of cured and uncured GAP was found to be similar.

This result was perplexing in light of earlier model compound studies which indicated the urethane region of the GAP to be substantially less stable than the backbone or terminal regions. The addition of more urethane cross-links to GAP should have produced a less stable gumstock. Preparation of other urethane model compounds showed that the higher-molecular-weight isocyanates produced a more stable urethane model compound relative to butyl isocyanate used in earlier model-compound studies.

Table II. Residual Tin vs. Stability and Cure Rate for Four Lots of GAP

GAP Lot	Tin Content (PPM)	Decomposition Rate (10^3 Hr^{-1})		Cure Rate (%NCO/Hr)
		Uncured	Cured	
11391-1	374	0.29	0.30	50.0
11391-2	250	0.32	0.27	148.6
1000-6	216	0.25	0.21	2.7
9961	5	0.22	0.18	0.5

GAP lot 9961 was selected for gumstock and propellant aging studies. One limitation of 9961 GAP was the slow rate of cure, which necessitated a fairly strong catalyst system to achieve reproducible gumstock and propellant cures.

Classes of propellant ingredients and impurities expected to create stability problems in GAP were screened in GAP lot 9961. Nitrogen evolution was measured for GAP combined with "destabilizers" stored at 105 to 125 C. Destabilizing elements included iron acetyl acetonate (FeAA), dinitrosalicylic acid (DNSA), nitric acid, phase-stabilized ammonium nitrate (PSAN), nitrate esters such as TMETN, copper-lead burning-rate catalysts such as LC12-6, and ammonium perchlorate (AP). The thermal stability of GAP lot 9961 in the presence of destabilizing additives is summarized in Table III. Soluble iron (FeAA), acids, TMETN, and ammonium nitrate (particularly NiO-PSAN) were all found to destabilize GAP lot 9961.

Table III. Additive Effects on GAP Lot 9961 Thermal Stability

Additive in GAP	Content, %	Decomp. Rate, 10^3 Hr^{-1}	
		Temp = 125C	Temp = 105C
None	-	0.2	<.1
FeAA	0.05	4.2	-
DNSA	0.05 5.0	0.2 1.2	-
HNO_3	0.5	1.0	-
H_2SO_4	0.7	0.7	-
AN (Pure)	20	1.0	-
AN (ZnO)	20	0.9	-
AN (NiO)	20	2.0	-
- - - - - - - -	- - - - - -	- - - - - -	- - - - - -
TMETN-AR[1]	50	-	0.8
TMETN-W[2]	50	-	0.7
TMETN-AR/AP	50/20	-	1.6
TMETN-AR/LC12-6	50/3	-	1.0
1,2: TMETN-AR = as recieved; TMETN-W = bicarbonate washed			

The effectiveness of candidate stabilizers to restore the stability of GAP mixtures containing destabilizing elements was studied. Mixtures of GAP and FeAA (0.05%), HNO₃ (0.5%), AN (20%), TMETN (50%), TMETN/LC12-6 (50/3%), or AP (40%) were tested for nitrogen evolution rates at storage temperatures of 105 to 125 C. Results of these tests are presented in Table IV. These data were compared and then compiled as to the most effective stabilizer types as a function of propellant ingredient system. This compilation is presented

Table IV. Stabilizer Effects in Mixtures of GAP Lot 9961 and Destabilizing Additives

ADDITIVE TYPE/CONTENT	STABILIZER TYPE/CONTENT		DECOMPOSITION RATE (10^3 Hr^{-1})
	STABILIZER TYPE	CONTENT, %	
FeAA/0.05%	None	-	4.2
	PROTECH 2725	0.6	0.2
	Al$_2$O$_3$/	1.0	3.8
	DER-331	1.0	4.9
	Epoxy 126	1.0	3.3
HNO$_3$/0.5%	None	-	1.0
	PROTECH 2725	1.0	0.6
	Al$_2$O$_3$	1.0	0.9
	DER-331	1.0	0.8
	MNA/NDPA	0.5/0.5	1.0
	Proton Sponge	1.0	0.3
	Al$_2$O$_3$/DER-331/PROTECH	0.33/0.33/0.33	0.8
AN (ZnO)/20%	None	-	0.9
	PROTECH 2725	1.0	1.1
	Al$_2$O$_3$	1.0	1.3
	DER-331	1.0	0.8
	MNA/NDPA	1.0	0.7
	DER-331/MNA/NDPA	1.0/0.5/0.5	0.3
	Al$_2$O$_3$/MNA/NDPA	1.0/0.5/0.5	0.6
	Al$_2$O$_3$/PROTECH 2725	1.0/1.0	0.1
TMETN/50%	None	-	0.8
	PROTECH 2725	0.7	0.6
	Proton Sponge	3.0	13.0
	MNA/NDPA	1.5/1.5	0.4
	ERL-4221	3.0	1.5
	DER-331	3.0	0.6
	Al$_2$O$_3$	1.5	0.7
	DER-331/Al$_2$O$_3$/MNA/NDPA	1.0/1.0/0.5/0.5	0.2
TMETN/LC12-6 (50/3%)	None	-	1.0
	PROTECH 2725	3.0	1.6
	Al$_2$O$_3$	3.0	0.5
	DER-331	3.0	0.6
	MNA/NDPA	1.5/1.5	0.5
	Proton Sponge	3.0	1.8
	Al$_2$O$_3$/DER-331/MNA/NDPA	1.0/1.0/0.5/0.5	0.2
AP/40%	With & Without Stabilizer	Variable	<0.1

Note: TMETN- and AP-containing mixtures tested at 105 C; others tested at 125 C

in Table V. The TMETN/LC12-6 system was found to be most difficult to stabilize, followed by TMETN alone. Owing to the higher level of instability, the TMETN-based mixtures were tested at 105 C rather than 125 C for the other systems. PROTECH proved an effective stabilizer in the FeAA and AN systems, but was incompatible with TMETN. Proton sponge was effective in acidic HNO3-containing systems, but was also incompatible with TMETN. Fumed alumina and DER-331 epoxy were partially effective in some systems, and ineffective in others. In certain cases, stabilizer blends (i.e., fumed alumina + PROTECH in the AN-containing system) were more effective than either stabilizer alone.

Table V. Summary of Effective Stabilizers in Various GAP Prepolymer Systems

Additive	Content (%)	Ranking[1]	Effective Stabilizers	Incompatible Stabilizers
TMETN/LC12-6	50/3	1	MNA/NDPA	Proton Sponge
			Al_2O_3	PROTECH 2725
			DER-331	
TMETN	50	2	MNA/NDPA	
			MNA/NDPA/Al_2O_3/DER-331	Proton Sponge
FeAA	0.05	3	PROTECH 2725	-
HNO₃	0.5	4	Proton Sponge	-
			PROTECH 2725	
			Epoxy (126)	
AN	20.0	5	-	-
AP	40	6	Al_2O_3	-

1. Most destabilizing (=1) to least destabilizing (=6) based on 125 and 105 C off-gassing in Lot 9961 GAP.

PROTECH 2725 was found to be highly effective in certain GAP mixtures, but incompatible in the TMETN-based systems. Based on recommendations from T. Rudy and B. Kosowski of MACH I (personal communications/1991), other PROTECH types offering improved compatibility with RONO₂ systems were evaluated, including 3120 and 8725. PROTECH 8725 was most promising. A comparison of PROTECHs 8725 and 2725 in various GAP mixtures is made in Table VI. PROTECH 8725 proved as effective or more effective than PROTECH 2725 in AP-, AN-, and FeAA-containing systems. In the TMETN-based system, PROTECH 8725 afforded some protection for the GAP mixture, whereas the original PROTECH 2725 was incompatible with GAP/nitrate ester mixtures.

Table VI. Comparison of PROTECH 8725 with PROTECH 2725

Mixture	Protech Type	Decomposition Rate (10^3 Hr[1])
Fe_2O_3/DBP/AP/GAP	-	0.5
Fe_2O_3/DBP/AP/GAP	8725	0.1
Fe_2O_3/DBP/AP/GAP	2725	0.2
AN/GAP	-	1.0
AN/GAP	8725	0.2
AN/GAP	2725	1.0
FeAA/GAP	-	4.2
FeAA/GAP	8725	0.2
FeAA/GAP	2725	0.3
TMETN/AN/GAP	-	2.1
TMETN/AN/GAP	8725	1.4
TMETN/AN/GAP	2725	

The effect of candidate stabilizers (specifically fumed alumina, DER-331, and PROTECH 8725) on the rate and quality of gumstock cures was evaluated. Fumed alumina and DER-331 were benign at concentrations of 1-percent (binder percent). PROTECH 8725 proved anything but benign with a substantial isocyanate demand and an ability to scavenge appreciable concentrations of the cure catalyst, dibutyl tin dilaurate. At normal -NCO/-OH cure ratios of 0.95/1.0 and catalyst contents of 15 to 50 ppm DBTDL, PROTECH 8725 effectively blocked the cure reaction. Combined with the inherently slow rate of cure associated with GAP lot 9961, gumstock cures were slow and incomplete. Increasing either the level of cure catalyst or the cure ratio resulted in gumstock cure. The quality of gumstock cure (qualitative tear tests) was superior when the catalyst levels rather than curative levels were increased. Unlike the unfilled gumstock systems, filled gumstock formulations were relatively insensitive to the presence of PROTECH 8725. Initial screening mixes of filled GAP gumstocks containing PROTECH 8725 provided acceptable cures at lower curative and catalyst concentrations.

In the above studies, a 50/50 blend of Desmodur N-3200 and HMDI gave superior tear properties over N-3200 alone. A multi-functional adduct of TMXDI and TMP was evaluated and gave significantly better strain and tear resistance than either N-3200 or the N-3200/HMDI blend. However, the TMXDI adduct exhibited a relatively slow reaction rate, and in combination with the slow-reacting GAP lot 9961, gave slow and variable cures. The 50/50 blend of N-3200 and HMDI was selected for subsequent aging studies.

STABILIZER EFFECTS IN GUMSTOCK AGING

Two binder formulations were selected to conduct investigations of stabilizer effects in unfilled GAP gumstocks. GAP plasticized with dibutylphthalate (DBP) was selected to represent a lower energy reduced smoke binder (RS), where "lower energy" compares to other GAP binders containing energetic plasticizers. A GAP/DBP binder still yields higher performance than standard butadiene-based binders. GAP plasticized with a TMETN/TEGDN blend was selected to represent a typical Class 1.3 minimum-smoke binder (MS). Table VII describes the mix matrix and target stabilizers for aging evaluations of the two binder types.

Table VII. Summary of Formulation and Stabilizer Packages for Aging Studies

Propellant Variable	Reduced-Smoke	1.3 Minimum Smoke
Polymer/Curative, %	GAP/N-3200/HMDI, 26.0	GAP/N-3200/HMDI, 20.0
Plasticizer, %	DBP, 2.0	TMETN/TEGDN, 10.0
Cure Catalyst	DBTDL	DBTDL
Oxidizer 1, % Oxidizer 2, %	AP (200/20µ); 70.0 -	AN (160/20µ), 50.0 HMX (1.5µ), 20.0
Rate Catalyst, %	Fe₂O₃, 2.0	-
Stabilizers	1) None 2) Fumed Alumina 3) PROTECH 8725	1) MNA/NDPA 2) PROTECH 8725/MNA/NDPA 3) Al₂O₃ (Fumed)/MNA/NDPA 4) DER-331/MNA/NDPA
Note: DBP = dibutylphthalate; DBTDL = dibutyl tin dilaurate		

Seven binder/stabilizer systems (three reduced-smoke and four minimum-smoke) were aged for 0,4,8,12, and 24 weeks at three storage temperatures including 70, 120, and 140 or 170 degrees F (the RS binders were aged at 170 degrees F while the MS binders were aged at 140 degrees F). Lower storage temperatures in the MS system were chosen to avoid the possibility of mechanism shift in the GAP/RONO₂ binder system[5].

Testing of the unfilled gumstocks included uniaxial and dynamic tensile, off-gas analysis, cube cracking, gel fraction, and crosslink density. 12-week test results are discussed below. 24-week test results are pending.

Two of the seven systems exhibited shifts in uniaxial tensile properties. These were the unstabilized and fumed alumina-stabilized reduced-smoke formulations. Both formulations exhibited higher strain, equivalent stress, and lower modulus (see Table 8). Shifts in the unstabilized reduced smoke binder were greater than in the fumed alumina system.

Three of the seven systems exhibited shifts in dynamic tensile properties (RMS). These were the unstabilized and fumed alumina-stabilized formulations in the reduced smoke system and the unstabilized minimum smoke formulation. All three formulations showed decreasing storage modulus indicative of reduced crosslink network. The fact that rupture stress was not affected suggests that these may be shorter, secondary crosslink sites that do not contribute to the ultimate binder strength.

Two-inch cube cracking specimens remain defect free. Dimensional increases (indicative of nitrogen gas evolution exceeding gas migration, which is a precursor to sample fissuring) were noted between the baseline and 4 week intervals, however, subsequent 8- and 12-week intervals have seen dimensional losses back to the baseline dimensions.

Nitrogen off-gassing data were not consistent with dimensional shifts in cracking-cubes. Nitrogen evolution levels were low at 4 weeks, but increasing at 8 and 12 weeks. Levels were independent of stabilizer content in the reduced-smoke system. In the minimum-smoke system, the unstabilized formulation exhibited higher levels of nitrogen evolution at 8 weeks, but similar levels after 12 weeks. This may indicate a stabilizer-driven induction period.

MNA concentrations were monitored. The DER-331- and PROTECH 8725-stabilized formulations exhibited a lower rate of MNA depletion than the unstabilized- and fumed-alumina-stabilized formulations (Figure 3).
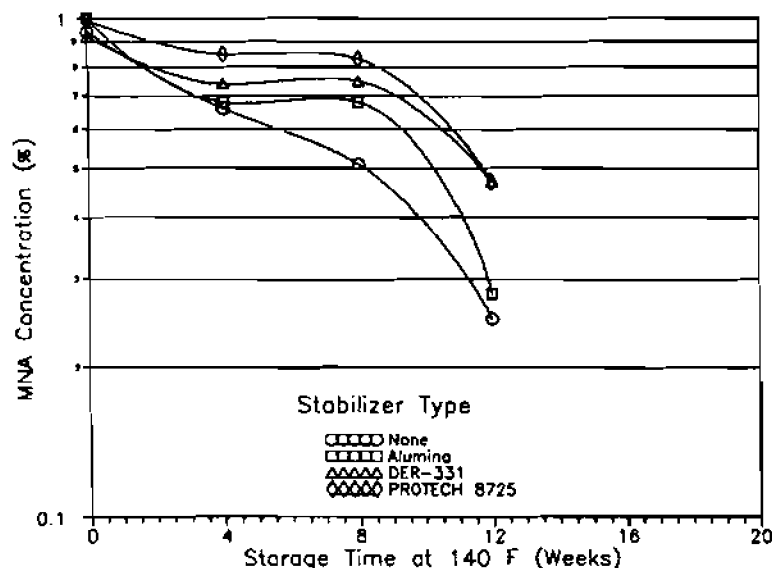

Figure 3. Stabilizer Effects on MNA Concentration of Unfilled Gumstock Aging Samples

Gel-fraction test results are described in figure 4. Two reduced-smoke formulations exhibited a consistent decrease in gel-fraction with time. These are the unstabilized- and fumed-alumina-stabilized formulations. These same shifts were also observed in crosslink density test results. Both sets of data indicate a loss of crosslink structure but, based on uniaxial tensile properties, these changes are relatively benign and do not appear to impact ultimate binder strength.

STABILIZER EFFECTS IN FILLED GUMSTOCK AGING

Stabilizer effects on the aging properties of filled GAP gumstocks have been studied through 12-weeks accelerated storage. This aging effort is continuing through 24 weeks. The matrix of storage temperatures, removal points, and tests were the same as the matrix for the unfilled gumstocks. The single variable change involved doping the unfilled gumstocks with typical propellant fillers. Curative content, catalyst content, plasticizer ratio, and stabilizer content were all maintained at the same concentrations used in the unfilled gumstocks. In the reduced-smoke system, 70 percent AP and 2 percent iron oxide were blended into the RS binder. In the minimum-smoke system, 50 percent PSAN (3% zinc-oxide) and 20 percent HMX were blended into the MS binder.

In addition to the normal aging samples and tests, additional samples from the RS binder were also prepared to evaluate humidity effects on aging properties. Samples of the AP/iron oxide-doped gumstocks were conditioned for 4 weeks under desiccated conditions and 4 weeks in 80-grains H_2O/lb dry air. At the completion of the conditioning period, samples were placed in vapor-seal aging bags, and introduced into aging.

Through 12 weeks accelerated aging, the filled GAP gumstocks have exhibited a general increase in stress and modulus without loss in strain capability. This toughening effect appears more pronounced in the reduced-smoke system. These data are presented in Table VIII. The toughening effect was independent of stabilizer type. Uniaxial tensile data from the 120°F storage condition exhibited only minor shifts from baseline properties. This result suggests that the toughening effect was not a post-cure phenomenon.
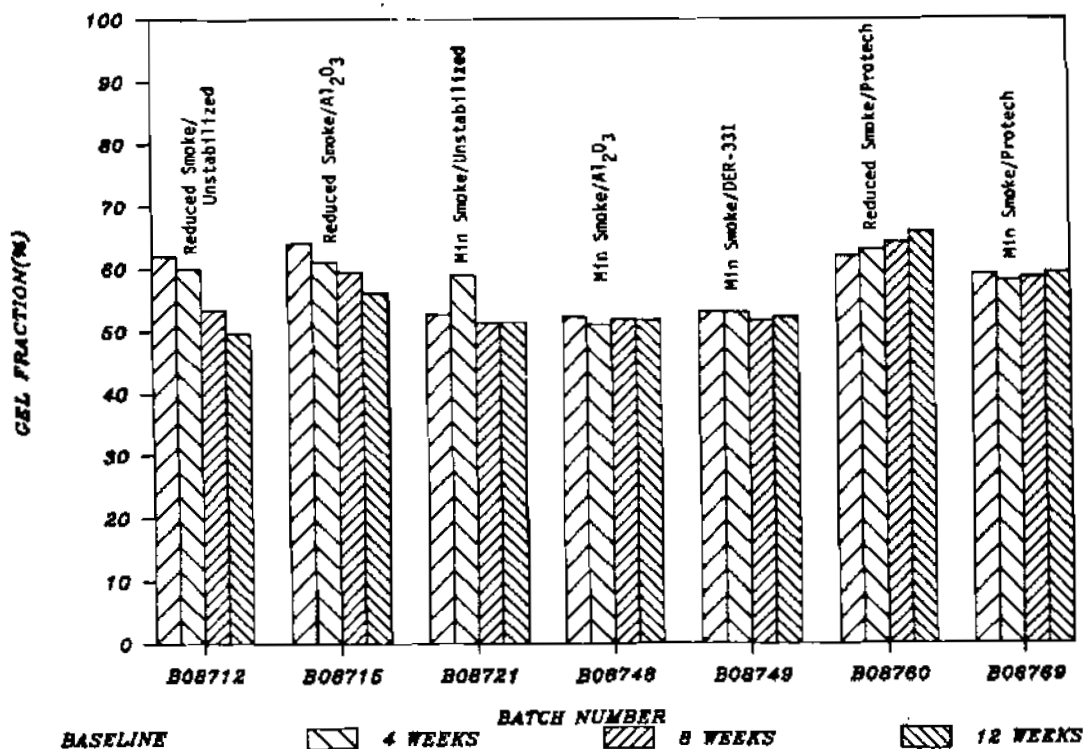
GEL FRACTION(%)

100
90
80
70
60
50
40
30
20
10
0

Reduced Smoke/Unstabilized — Reduced Smoke/Al$_2$O$_3$ — Min Smoke/Unstabilized — Min Smoke/Al$_2$O$_3$ — Min Smoke/DER-331 — Reduced Smoke/Protech — Min Smoke/Protech

B08712   B08715   B08721   B08748   B08749   B08760   B08769

BATCH NUMBER

BASELINE   4 WEEKS   8 WEEKS   12 WEEKS

Figure 4. Gel-fraction Results for the Unfilled-Gumstock Aging Samples

Table VIII. Uniaxial Tensile Results for Filled-Gumstock Aging

Formulation/Aging Variables		Baseline	4 Week	12 Week	
		170/140 F	170/140 F	170/140 F	120 F
Batch No. 8952 (RS/No Stab)	stress, psi	87	136	142	95
	strain, %	26	31	33	30
	stress, psi	408	509	495	353
Batch No. 8953 (RS/Al$_2$O$_3$)	stress, psi	84	136	151	93
	strain, %	31	35	35	32
	stress, psi	289	455	509	321
Batch No. 8954 (RS/Protech)	stress, psi	118	152	160	131
	strain, %	21	22	21	22
	stress, psi	709	894	1013	743
Batch No. 8923 (MS/No Stab)	stress, psi	70	88	92	80
	strain, %	39	42	39	39
	stress, psi	221	275	297	269
Batch No. 8908 (MS/Al$_2$O$_3$)	stress, psi	67	75	83	82
	strain, %	60	52	54	49
	stress, psi	139	175	195	233
Batch No. 8895 (MS/DER-331)	stress, psi	66	98	110	95
	strain, %	38	43	57	42
	stress, psi	233	277	194	268
Batch No.8924 (MS/Protech)	stress, psi	90	106	105	94
	strain, %	26	26	24	29
	stress, psi	583	620	658	465

RS = Reduced Smoke (aged at 170 and 120 F)
MS = Minimum Smoke (aged at 140 and 120 F)

Samples prepared to evaluate humidity effects on the aging properties of the reduced smoke system are currently in accelerated aging. Four-week exposure in a desiccated environment versus four-week exposure in a humidified environment was found to have little or no effect on resultant tensile properties in baseline testing. These interim results are detailed in Table IX.

Table IX. Humidity Effects on Pre-aging Tensile Properties

Propellant Batch No.	8843		8853		8854	
Stabilizer Type	None		Fumed Alumina		PROTECH 8725	
Humidity Conditioning	Desic.	80 Grains	Desic.	80 Grains	Desic.	80 Grains
70 F Stress, psi	82	78	102	90	115	110
70 F Strain Max/Rup, %	20/22	19/21	36/37	35/38	13/14	12/13
70 F Modulus, psi	527	558	328	302	1133	1187

Note: Samples conditioned 4-weeks under desiccated or humidified (80-grains moisture) chamber

CONCLUSIONS

GAP lot 9961 is relatively stable, due to a low residual tin concentration. This type of high purity GAP appears to age well in the presence of typical propellant ingredients such as AP, iron oxide, TMETN, AN, and HMX. Candidate stabilizers, especially PROTECH 8725, have a significant stabilizing effect on GAP binder in laboratory studies, and appear beneficial in limited propellant aging studies. With or without stabilizers, GAP lot 9961 yields tougher aged propellants (higher stress and modulus without loss in strain capability). Additional aging data are needed to extend this data base.

Interim findings from the program are categorized below according to the major program tasks

Model compound studies conducted at 3M showed the following:

1. Thermal decomposition of pendant azide groups within the GAP molecule proceed independently of azide location.
2. Thermal decomposition is slower in air than in argon atmosphere
3. Decomposition products from the urethane model were different from backbone and alcohol decomposition products, mostly dimers and trimers of the parent compound.
4. Structure of isocyanate curatives used in GAP propellants appears to effect the stability of the overall GAP binder (i.e., butyl- vs octadecyl-isocyanate)

Stabilizer studies at 3M and ARC showed the following:

5. GAP stability is proportional to its purity and correlates directly with residual tin content.
6. Cured and uncured GAP exhibit similar stability
7. GAP stability can be driven largely by propellant ingredients, with greatest destabilization from RONO2 and soluble metals like iron and nickel (zinc appears relatively benign).
8. Stabilizers can block the effects of destabilizing propellant ingredients.
9. Stabilizer blends can be more effective than either stabilizer alone.
10. PROTECH 8725 is a very promising stabilizer, especially for non-nitrate ester systems, but disruptions to cure kinetics may limit its usefulness.
11. DER-331 and fumed alumina appear less effective, but do not pose the cure kinetics problems.

Aging studies at ARC showed the following:

12. Aging effects involve higher stress and/or modulus without loss in propellant strain capability.
13. Aging effects are more pronounced in the unstabilized baseline and in the fumed-alumina stabilized formulation.
14. 4-week exposure to high humidity had no effect on tensile properties of the AP/iron oxide formulation.

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